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Stratospheric Ozone Reactive Chemicals Generated by Space Launches Worldwide

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1. Introduction

Understanding and assessing the environmental impact of space launch operations has been a matter of public interest and statute since 1969. With the advent of large aluminum–ammonium perchlorate based solid rocket motors for the Shuttle, there has been particular interest in determining the transient and long term impact of the inorganic chlorine compounds and aluminum oxide particle components of rocket motor exhaust on stratospheric ozone depletion[1]. Environmental impact analysis updates of the Titan IV–Solid Rocket Motor Upgrade (SRMU) program are forthcoming. The recent Statement of Need from Materiel Command to understand the stratospheric impact of solid rocket motors, passage of the Clean Air Act Amendments in 1990, and the Montreal Protocol on Ozone Depleting Chemicals (ODCs) create new interest in developing a better understanding of the impact of inorganic chlorine compounds and aluminum oxide particles on stratospheric ozone concentrations. This report has three objectives:

- Tabulate the release of inorganic chlorine compounds in the atmosphere on a per launch and per year basis for space launch vehicles and ballistic missiles. The tabulation will have two main segments: the troposphere (0–15 km), and the stratosphere (15–50 km) and above. This report will focus on stratospheric effects. Additional information showing the altitude dependence of these releases is given for specific launches in the Appendix.

- Describe stratospheric ozone chemistry and elucidate important issues that require resolution. Among the open questions is the time dependence of the ozone depleting effect of inorganic chlorine compounds released in space launch in relation to that of organic ODCs. As defined in the Clean Air Act, ODCs are chemicals that have very long lifetimes in the atmosphere and, upon photolysis or reaction in the stratosphere, generate inorganic chlorine (and bromine) compounds that enter into catalytic ozone depleting cycles.

- Compare ozone depletion of inorganic chlorine compounds released by space launch vehicles and ballistic missiles with the ozone depletion caused by organic and inorganic chlorine and bromine released by other Air Force and worldwide activities.

Ozone depletion by inorganic chlorine may be enhanced by aluminum oxide (Al_2O_3, alumina) particles[1-7]. At this time there is insufficient evidence to confirm or refute this hypothesis. This report adds as an objective to tabulate the atmospheric emissions of aluminum oxide by launch vehicles and ballistic missiles.

1.1 Definition of Inorganic and Organic Chlorine (and Bromine) Compounds

Within the context of this report, inorganic chlorine compounds include hydrogen chloride (HCl), atomic and molecular chlorine (Cl, Cl_2), chlorine oxides (ClO, Cl_2O_2, OClO, and ClOO), hypochlorous acid (HOCl), and chlorine nitrate ($ClONO_2$). A similar set of inorganic bromine compounds also play a role in stratospheric chemistry. These compounds are linked by rapid reversible reactions in the ambient stratosphere, with lifetimes of seconds to weeks depending on the altitude, season, and time of day, and enter directly or indirectly into the catalytic ozone depletion

cycles. HCl and $ClONO_2$ are "reservoir compounds" with lifetimes of days to weeks in the ambient mid-latitude mid-altitude stratosphere.

Organic chlorine compounds such as the chlorofluorocarbons (CFCs) have one or several carbon-chlorine bonds. Organic chlorine compounds of concern here are the ODCs with atmospheric lifetimes of fractions of a year to hundreds of years (Class II and Class I ODCs). Their carbon-chlorine bond is severed in the stratosphere by solar photolysis or reaction. Once the carbon-chlorine bond is broken, the chlorine becomes "inorganic", and enters the catalytic ozone destruction cycle.

The nomenclature for inorganic and organic bromine compounds (such as Halons) is similar to that of chlorine compounds. In general, the inorganic bromine compounds are more reactive toward ozone than chlorine compounds.

1.2 Solid Rocket Motor Exhaust

Solid rocket motor performance and simulation codes often report the exit plane composition of the exhaust, with the chlorine largely appearing as HCl in the hydrogen (H_2) and carbon monoxide (CO) rich–reducing atmosphere of the combustion chamber. Afterburning in the near plume, in which the excess hydrogen and carbon monoxide react with ambient oxygen, leads to an altitude dependent multi-step conversion of the HCl into a time-varying mixture of inorganic chlorine compounds including HCl, Cl, Cl_2, ClO, Cl_2O_2, OClO, and ClOO[8].

The Aerospace Corporation is currently investigating several aspects of the temporal and spatial “transient” interaction of rocket plumes with the stratospheric ozone. This report focuses on the long term impacts of solid rocket exhaust on stratospheric ozone depletion.

1.3 Contents of the Report

Section 2 summarizes data on launch activities involving solid rocket motor systems projected to the year 2010 using current mission models. Since data are categorized by launch vehicle type, long-range estimates can be modified as launch rates change. Data and long range projections are given for Air Force, NASA, and U.S. commercial activities, for the European Space Agency (ESA) Ariane 5 due to enter service in 1995–1996, and the National Space Development Agency of Japan (NASDA) H-2, which entered service in 1994. Data on ballistic missile test rates are currently not available. This report shows their impact to be small compared to that of the heavy launch vehicles including Titan IV, Ariane 5, and the Shuttle.

Section 3 is a brief summary of stratospheric ozone chemistry, focusing on the well-established catalytic effect of inorganic chlorine compounds on stratospheric ozone depletion. It compares the time scales for ozone destruction associated with inorganic chlorine released by rockets to that of organic chlorine compounds and bromine compounds (which are ODCs).

Section 4 summarizes and projects data on ODC use by the Air Force Material Command. The dramatic projected reductions in ODC use are driven by an Air Force policy of environmental leadership and influenced by U.S. and international law, including the Clean Air Act Amendments of 1990 and the Montreal Protocol. These efforts reflect public understanding of the relationship of stratospheric chlorine to ozone depletion.

In Section 5 the relative ozone depletion from space launch activities is compared with that from ODC use.

2. Tabulation of Inorganic Chlorine and Aluminum Oxide Deposition in the Troposphere and Stratosphere by Launch Vehicles

The Aerospace Corporation rocket performance and flight simulation code estimates the rate of rocket propellant consumption as a function of altitude for U.S. launch vehicles and ballistic missiles and predicts the immediate composition of the exhaust plume[9]. The amount of inorganic chlorine and aluminum oxide deposited as a function of altitude is calculated from:

- payload requirements and launch trajectory
- ammonium perchlorate and aluminum loading of each solid rocket motor
- the known overall composition of the propellant exhaust

The Appendix presents results in 5 km altitude segments from the tropopause to solid rocket burn-out for the following vehicles: Delta II, Atlas IIAS, Titan IV and the Shuttle. Tropospheric data are included for the Delta and Atlas. The level of detail in the Appendix is informative and will be useful for future modeling studies.

The trajectory and propellant burn rate of each vehicle depends to some extent on the payload and mission. The launch-to-launch differences show up most clearly when the data are divided into 5 km altitude intervals as in the Appendix. The total deposition in the stratosphere versus troposphere will only change by a few percent at most with each launch; the uncertainty introduced by this variability is much smaller than that in the chemical model and insignificant compared to the inaccuracies in the projected launch rates. The tabulated numbers are for a typical mission and payload.

This report focuses on establishing the mass of inorganic chlorine compounds and aluminum oxide deposited above the tropopause. Although the height of the tropopause varies with temperature and atmospheric conditions it is assumed to be constant at 15 km for the purposes of this report. Table 1 presents the deposition in the troposphere, 0–15 km, and above for Titan IV and Titan IV–SRMU, Atlas IIAS, Delta II, MX (Peacekeeper) and Minuteman III, the Pegasus/Taurus, the Space Shuttle, the ESA Ariane 5, and the NASDA H-1 and H-2 launchers, in units of tons (2000 lbs/ton)[1,5,6,9]. The Ariane 5 is a heavy launch vehicle, comparable to Titan IV, with an ambitious launch schedule of 11 launches per year. The stratospheric data from Table 1 is presented graphically in Figure 1.

Some clarification is needed here about the Pegasus/Taurus vehicle. Pegasus is launched from an aircraft very near the tropopause (above 12 km); thus it is assumed that all of its propellant is burned in the stratosphere. Taurus upper stages are identical to Pegasus, but Taurus uses a Peacekeeper first stage and is launched from the earth's surface. The two vehicles are completely solid-fueled and are expected to deliver similar amounts of chlorine and alumina to the stratosphere. Taurus also deposits these exhaust components in the troposphere. Neither vehicle has a regular launch schedule yet.

Table 1. Inorganic Chlorine and Alumina (Tons per Launch) from Launch Vehicles

Vehicle	Chlorine (altitude, km) 0-15 Troposphere	15-60 Stratosphere	0-60 Total Exhaust	Alumina (altitude, km) 0-15 Troposphere	15-60 Stratosphere	0-60 Total Exhaust
Titan IV	78	48	126	111	69	180
Titan IV w/ SRMU	90	55	145	128	93	221
Delta II	17	8	25	24	12	36
Atlas IIAS	6	3	9	9	5	14
MX	na	6	na	na	9	na
MM III	na	2	na	na	3	na
Pegasus/Taurus	0/10	4	4/14	0/15	5	5/20
Shuttle	147	79	226	209	112	321
Ariane 5	50	57	107	71	81	152
H 1	6	3	9	9	4	13
H 2	22	11	33	31	16	47

A number of familiar launch vehicles are not represented in the Appendix and Table 1 because they do not currently use solid rocket motors. They include the Russian Proton and Energia, and the Chinese Long March series. Roughly half (seven per year) of the Ariane 4 launches use two solid strap-ons, giving it a total chlorine loading one-half the Atlas IIAS, but these motors burn out in the troposphere.

Further, data on most foreign ballistic missiles are absent, as are data on U.S. Navy missiles. If we obtain data on Soviet ballistic missile launch exhaust profiles or launch rates, they will be incorporated in the future. Unless the ballistic missiles are heavily used for space launch, they are likely to make a small contribution compared to the heavy launch vehicles such as the Titan IV, Shuttle, and Ariane 5.

There are many other classes of solid rockets used for tactical missions such as ground-to-air, air-to-air, and air-to-ground attack, and others considered for the antiballistic role. Because they rarely enter the stratosphere, they are not considered.

There is a trend to consider using demilitarized ballistic missiles for space test, and another to develop new solid rocket systems for space launch. The DOD and NASA are currently investigating new expendable launch vehicle systems, including concepts using solid propellant upper stages. These would burn substantially above 50 km, exposing the upper atmosphere to solid rocket propellant exhaust. If new programs materialize and mission models call for significant contributions, they will be considered in a follow-up report.

Data on alumina particle deposition (shown in Table 1) are provided for completeness. The effect of alumina particles on stratospheric ozone depletion is yet unknown. Issues being investigated include their ability to act as catalytic sites for ozone decomposition (direct destruction) as reported in the literature[2,3], and their potential for supporting catalytic reaction with the reservoir species HCl and $ClONO_2$, analogous to the process that occurs in polar stratospheric clouds[10].

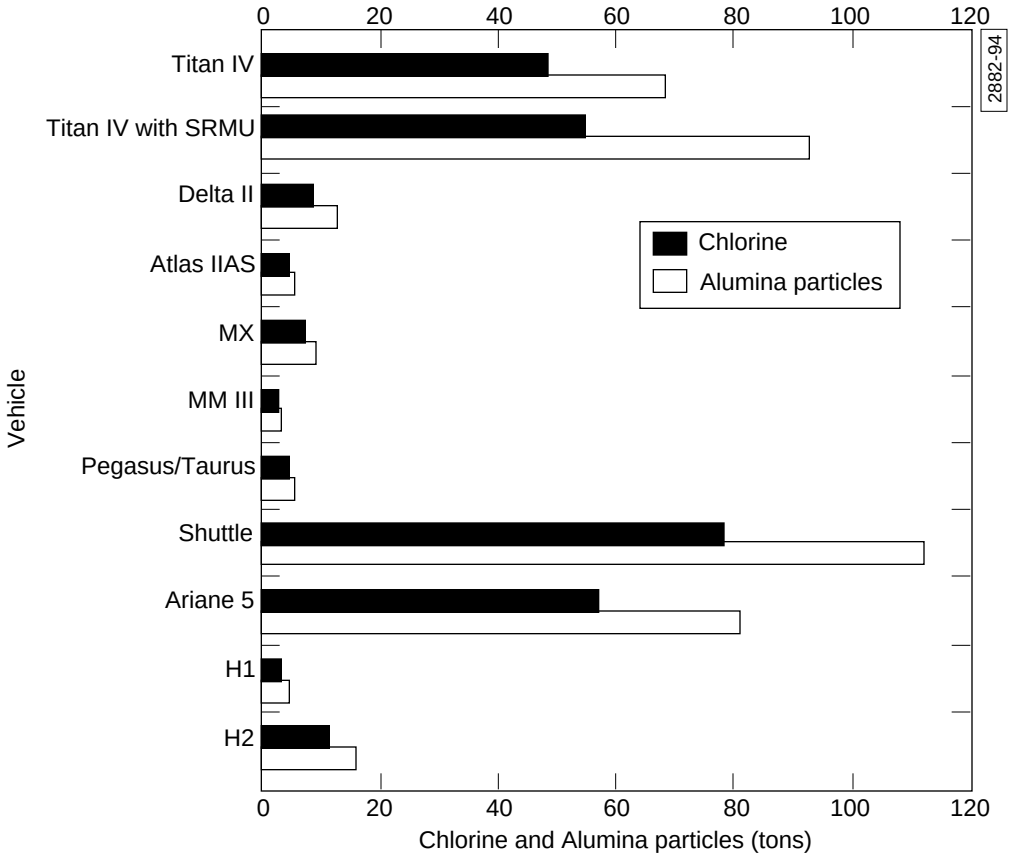


Figure 1. Chlorine and alumina particles deposited in the stratosphere by launch vehicles, per launch.

The exhaust aluminum oxide particles also contain iron and chlorine, which may make them more reactive. The exact chemical nature, as well as size distribution (and total surface area) of particles formed in rocket exhaust in the stratosphere is currently unknown. Preliminary experiments at Aerospace by L. R. Martin indicate that plausible particle compositions give highly variable rates of direct ozone destruction. Investigations of the kinetics of alumina exhaust particulate catalyzed reactions are continuing at Aerospace and at several other sites.

Table 1 also shows the corresponding amounts of inorganic chlorine and aluminum oxide particles exhausted into the troposphere, the layer of the atmosphere closest to the earth. As discussed more fully in Section 3, these deposits have an insignificant impact on stratospheric ozone depletion because they are water soluble materials or rapidly react in the troposphere to form water soluble products or particles, and would be washed out of the atmosphere by rain in a time much shorter than

the transport time from the troposphere to the stratosphere. The last column of Table 1 gives the total amounts of chlorine and aluminum oxide in the exhaust of each launch vehicle that are generated when all propellant in the vehicle is burned.

Launch rates for government and commercial missions are shown in Table 2. The actual number of launches is given for 1991–1993; the 1994–1997 column shows the projected average rate[9,11,12,13]. These sources differ in that some classify launches by the owner of the payload, others by the owner of the booster. The data in the last column is a projection based on the National Mission Model, 1998–2010.

Tables 3 and 4 present an estimate of the annual deposition of chlorine and alumina particles for the period 1991–2010. The sources considered are Air Force, NASA, U.S. commercial, and foreign launches, broken down by type of vehicle and launch year. These numbers are derived by multiplying the mass of the exhaust products deposited in the stratosphere for each vehicle type (shown in Table 1) by the respective launch rate (shown in Table 2). These tables estimate the total extent and rate of deposition useful for determining the cumulative environmental impact of each program. The U.S. National Environmental Policy Act (NEPA) requires that federal organizations understand and mitigate their environmental impact, including cumulative impact.

Several caveats are in order for Tables 3 and 4. The Ariane 5 will not fly until 1995–1996, and it is not known if all launches will be Ariane 5, or if some Ariane 4s will still be used. The numbers shown for 1995–1997 and 1998–2010 were reached by assuming complete conversion to the Ariane 5 in mid-1995 and thus represent upper limits. The numbers shown for the Titan IV for 1995–1997 are for the current flight configuration. We assume that Solid Rocket Motor Upgrade (SRMU) development will be complete at the end of 1997. The numbers presented for the period 1998–2010 assume exclusive use of Titan IVs equipped with the SRMU. The new design will deposit 12 percent more chlorine and 34 percent more alumina particles into the stratosphere. The data in Tables 3 and 4 give an idea of the extent of the future deposition rate, and are useful for planning purposes. Currently, military and civilian government launches release about one-half to one-third as much inorganic chlorine in the stratosphere as commercial launches. This scenario will change dramatically when Ariane 5 becomes a major commercial launch vehicle.

The total projected inorganic chlorine and aluminum oxide flux to the stratosphere from all types of vehicles and organizations for the years 1998–2010 is presented in the last column of Tables 3 and 4. The numbers presented are yearly averages over the entire period.

As previously stated, the numbers shown for the last period are based on projections. Given the length of time and number of variables involved, the accuracy of the projection is unknown. Judging by past comparisons of projected and actual launch rates, the launch projection is probably optimistic;

Table 2. Launch Activity by Sponsor (Launches Per Year)

	1991	1992	1993	1994–1997	1998–2010
Air Force					
Titan IV	2	1	1	3	4.5
Delta II	1	6	6	8	8
Shuttle	2	1	0	0	0
Total	5	8	7	11	12.5
NASA					
Shuttle	4	7	7	8	8
Total	4	7	7	8	8
Commercial					
Delta II	4	3	1	5	5.5
Atlas II AS	0	1	1	1	2
Total	4	4	2	6	7.5
Foreign					
Ariane	8	7	7	8	8
H 1	1	1	0	1	1
H 2	0	0	0	1	1
Total	9	8	7	10	10
World Total	22	27	23	35	38

actual launches might be less frequent because of various unforeseen complications. Regardless, it is essential to look ahead a decade or more, given the rate at which space launch systems evolve. It might be reasonable to assume a 7- to 15-year cycle for the development of a new heavy launch vehicle based exclusively on liquid propellants and perhaps longer to develop alternative solid propellant formulations that are free of either chlorine compounds or metals, or both. Thus, in the research and development of advanced propulsion systems, it is important to consider stratospheric ozone depletion, even while the observational, kinetic, and modeling efforts continue to establish the scope and impact of deposition of chlorine and alumina particulates by launch vehicles.

Table 3. Annual Stratospheric Deposition Rates (Tons per Year) for Inorganic Chlorine for U.S. and Foreign Launches 1991–2010

Launches	1991	1992	1993	1994–1997	1998–2010
Air Force					
Titan IV	97	48	48	145	247
Delta II	8	51	51	67	67
Shuttle	158	79	0	0	0
Total	263	178	99	212	314
NASA					
Shuttle	316	553	553	631	631
Total	316	553	553	631	631
Commercial					
Delta II	34	25	8	42	46
Atlas IIAS	3	4	4	4	7
Total	34	29	12	46	53
Foreign					
Ariane	0	0	0	228	456
H 1	3	3	0	3	3
H 2	0	0	0	11	11
Total	3	3	0	242	470
World Total	616	763	664	1131	1468

Table 4. Annual Stratospheric Deposition Rates (Tons per Year) for Alumina Particles for U.S. and Foreign Launches 1991–2010

Launches	1991	1992	1993	1994*–1997	1998–2010
Air Force					
Titan IV	138	69	69	206	419
Delta II	12	72	72	96	96
Shuttle	225	112	0	0	0
Total	375	253	141	302	515
NASA					
Shuttle	450	787	787	900	900
Total	450	787	787	900	900
Commercial					
Delta II	48	36	12	60	66
Atlas IIAS	0	5	5	5	10
Total	48	41	17	65	76
Foreign					
Ariane	0	0	0	650	650
H 1	4	4	0	4	4
H 2	0	0	0	16	16
Total	4	4	0	670	670
World Total	877	1085	945	1937	2161

3. Stratospheric Ozone Chemistry of Launches: Plume Chemistry and Ozone Destruction

Hydrogen chloride (HCl) is a major combustion product of solid rocket boosters that use ammonium perchlorate as an oxidizer. As the gases leave the motor, national standard plume models run at Aerospace and elsewhere indicate that afterburning occurs[8,14,15]. In this afterburning region, a substantial amount of the HCl (21–74 percent, depending on altitude) is predicted to be converted to C1 through reactions such as:

$$HCl+OH = Cl+H_2O \quad (1)$$

and others. Most of the C1 atoms combine in the cooler post-afterburning region of the plume to produce molecular chlorine. The distinction between molecular chlorine and atomic chlorine is not significant for daytime launches however, because it rapidly photolyzes to again liberate chlorine atoms:

$$Cl_2+light = 2Cl \quad (2)$$

The free chlorine atoms produced in a launch vehicle's exhaust can immediately react with ozone in the stratosphere through the widely accepted mechanism for ozone destruction by chlorine:

$$Cl+O_3 = ClO+O_2 \quad (3)$$

$$O+ClO = C1+O_2 \quad (4)$$

Since chlorine atoms that are initially consumed by reaction 3 are later released through reaction 4, the net result of the two reactions is:

$$O+O_3 = 2O_2 \quad (5)$$

This results in the destruction of ozone with no net loss of the chlorine required to cause the destruction. Chlorine liberated through reaction 4 is then available to restart the destruction cycle. This reaction sequence 3–4 is referred to as the 'normal' catalytic ozone destruction cycle.

Ultimately, the chlorine atoms will react with hydrogen-containing molecules such as methane:

$$Cl+CH_4 = HCl+CH_3 \quad (6)$$

One of the authors (L. R. Martin) has suggested that another ozone destruction cycle may occur in the

lower stratosphere (~20 km)[16]:

$$Cl+O_3 = ClO+O_2 \quad (7)$$

$$ClO+ClO = Cl_2O_2 \quad (8)$$

$$Cl_2O_2+\text{UV light} = Cl+C1OO \quad (9)$$

$$ClOO+M = Cl+O_2 \quad (10)$$

The result of reactions 7–10 is a process that effectively converts ozone into molecular oxygen:

$$2\ O_3 = 3O_2 \quad (11)$$

This reaction sequence is postulated due to the abundance of C1O that might result from reaction 3 in the wake of a solid rocket motor. A zero-dimensional calculation predicts an ozone "hole" with a diameter of tens of kilometers at an altitude of 30 km, depending on the rate of dispersion of the plume [16].

Although the basic chemical processes described above are well established, it is important to recognize that there has been only one reported in-situ measurement of ozone depletion from a launch. This observation was for a U-2 flight through the plume of a Titan III vehicle at an altitude of 18 km 13 minutes after launch. The measurement did not provide the scale of the ozone depletion, but a drop in ozone density by 40 percent was reported[17]. The effects predicted above are expected to continue to develop for several hours after launch.

3.1 Comparison with Ozone Destruction by Organic Chlorine Compounds

To understand adequately the potential impact of the launch-related effects described above, we describe here the ozone destruction caused by organic chlorine compounds, represented by CFCs. These compounds are generally very inert in the atmosphere and survive for tens of years without undergoing chemical reaction. Upon reaching the stratosphere, they become photolyzed by ultraviolet light from the sun that does not penetrate to lower altitudes:

$$CFC+\text{UV light} = Cl+\text{organic radicals} \quad (12)$$

This photolysis releases atomic chlorine that participates through reactions 3–4 in the destruction of stratospheric ozone. Because the organic compounds reach the stratosphere only slowly, the effects are global in nature and enduring.

Because the extremely low temperatures in the Antarctic favor the formation of Cl_2O_2 (reaction 8), this chlorine can also contribute to stratospheric ozone depletion there through reactions 7–10. This

is the process assumed responsible for the Antarctic ozone hole that appears and grows larger each year[10].

Worldwide use of CFCs over the last several decades has resulted in the introduction of about 25 million tons of CFCs to the atmosphere[5]. From this, about 300,000 tons of atomic chlorine are produced in the stratosphere each year by photolysis (reaction 12). Due to the long atmospheric lifetime of the CFCs, the production of atomic chlorine in the stratosphere from this source is expected to continue for many decades into the future and will persist long after manufacturers have stopped producing these chemicals.

In comparing the effects of inorganic chlorine deposited in the stratosphere by solid rocket motors with those of organic chlorine sources, it is important to consider the relevant time scales. Solid rocket motors deposit inorganic chlorine directly into the stratosphere at all altitudes within a small volume. Organic chlorine materials survive for decades in the troposphere and slowly migrate to the stratosphere where they are converted through photolysis into inorganic chlorine. Once the CFCs are photolyzed and the launch vehicle plume has dispersed, both sources of inorganic chlorine behave similarly and will effect stratospheric ozone depletion over the next several years.

3.2 Aluminum Oxide Particle Effects

The discussion above does not consider the potential effects of particulate exhaust of the solid rocket motors. These effects were considered as part of the 1991 Scientific Assessment of Stratospheric Ozone[5], but the heterogeneous chemistry that might take place on aluminum oxide and aluminum oxychloride particles is unknown[2,3]. Some proposed effects are:

- destruction of ozone by surface catalysis
- catalysis of the photolysis of CFCs
- catalysis of reactions of “reservoir" species, such as $C1NO_3$, to liberate reactive chlorine:

$$C1NO_3 + HC1 \xrightarrow[\text{particles}]{} C1_2 + HNO_3 \qquad (13)$$

Before the effect of these particulates on stratospheric ozone depletion can be assessed, more investigation is required. As stated earlier, this report tabulates the mass of aluminum oxide emitted in the stratosphere by a variety of launch vehicles. These data will be useful for future predictions once the reactivity and effective surface area of the particles is better understood.

4. Use of Ozone Depleting Chemicals

Rocket launches are not the only source of inorganic chlorine in the stratosphere. As pointed out in Section 2, the main source of stratospheric chlorine is CFCs. The Air Force uses CFCs as refrigerants, fire suppressants, and cleaning solvents. The use of such chemicals has declined in recent years in response to Air Force policy. Table 5 shows the total tonnage of organic chlorine compounds used by SMC; its parent organization, the Air Force Materiel Command (AFMC); and the world. Actual tons used are shown for calendar years 1991–1992, while projected use is shown for 1993–2000. The numbers used here include CFCs, halons, carbon tetrachloride, methyl chloroform, and HCFC-22. The ozone depletion potential (ODP)* of these compounds vary from 0.1 to 16.

A more accurate reflection of the ozone damage from these releases would be to weight the tons released for each compound by the corresponding ODP. The average ODP for emissions can be determined by dividing the ODP weighted emission by the total mass of emissions. The ODP weighted emission is the sum of the mass of each ODC[18,5] multiplied by its ODP. For SMC, the average ODP is 0.87; for the world, the average ODP is 0.54. The appropriate data are not available for AFMC. The equivalent ODP appropriate for the inorganic chlorine from rocket exhaust while controversial is about 1.3[19]. An ODP-weighted release rate will be included for all categories in an updated report when the data become available. We also intend to include the relevant data for the entire Air Force and the U.S.

An important trend to note is the continuing decrease in the use of organic chlorine compounds by SMC[18], AFMC[20], and the world[5], measured in both total tonnage and total stratospheric impact. These decreases are driven by federal law, Air Force policy, and international law.

Table 5. Use of Ozone Depleting Chemicals

Year	SMC (tons)	AFMC(1) (tons)	World (tons)
1991		1400	2,019,000
1992	29	1120	2,049,000
1993	51	700	1,639,000
1994	51	100	1,639,000
1995	24	24	1,081,500
1996	8	8	1,081,500
1997	8	8	731,500
1998	8	8	731,500
1999	8	8	731,500
2000	0	0	320,000

(1) includes SMC

* The ODP is defined as the steady state ozone depletion caused by a given mass of a compound released at the earth's surface at a constant rate relative to CFC-11 ($CFCl_3$) which, by definition, has an ODP of one. Factors influencing the ODP are the amount of halogen (chlorine or bromine) a compound contains, the fraction of the compound that reaches the stratosphere, and how efficiently the halogen released destroys ozone. Bromine is much more effective than chlorine at destroying ozone.

5. Comparison of Chlorine from Rocket Exhaust with Chlorine from Use of Ozone Depleting Chemicals

The results presented in Table 3 are charted in Figure 2. Table 3 and Figure 2 show a definite increase in the inorganic chlorine deposited in the stratosphere by launches with time. By the beginning of the next century, projected space launches will contribute twice as much inorganic chlorine to the stratosphere annually as launches do now. Even if the projected launch rates are optimistic, the upward trend is clear. During the same time period, ODCs released into the atmosphere from other sources will be decreasing significantly, as required by law. Manufacture of organic chlorine compounds, which currently accounts for 300,000 tons of stratospheric inorganic chlorine produced by photolysis annually[21], has already been scaled back and will be eliminated by 1996 except for a handful of essential uses. Natural sources of stratospheric chlorine contribute ten to one hundred times less chlorine than manufactured organic chlorine compounds[22,23,24]. Because the atmospheric lifetime of a typical CFC is 50–100 years, the backlog of accumulated CFCs in the atmosphere will continue to contribute close to 300,000 tons of inorganic chlorine annually well into the next century (see Figure 3). This annual contribution is not projected to drop to half its current level until between 2050 and 2100. This means that projected launch-generated inorganic chlorine will rise to a level approaching 0.5 percent of the annual level introduced by the backlog of accumulated CFC. However, new anthropogenic releases of chlorine, while still a small fraction of what is stored in the atmosphere, will soon be dominated by launch generated inorganic chlorine.

A comparison of the stratospheric chlorine loading from rocket exhaust with organic chlorine compound use should put the situation in perspective. These numbers are shown graphically for AFMC in Figure 4. It is clear that while use of organic chlorine compounds currently dominates the Air Force annual contribution to atmospheric chlorine that will reach the stratosphere, that component is rapidly decreasing. On the other hand, chlorine from rocket exhaust is remaining steady or increasing slightly. Thus, new contributions to atmospheric chlorine compounds that ultimately destroy ozone are projected to be dominated by space launches. A comparison of Tables 3 and 5 shows that transition from chlorine release dominated by organic chlorine compounds to chlorine release dominated by inorganic chlorine from rocket exhaust will occur in 1994 for AFMC. Worldwide, this transition will occur sometime after the year 2000.

An important point to make when comparing inorganic chlorine in the atmosphere from CFCs with that from rockets is the difference in the timescale due to the different lifetime of the sources. CFCs released at sea level require one to two years to reach the stratosphere. CFCs have lifetimes of 50 to 100 years, so the active chlorine generated by this CFC release will continue to build up for several years. Subsequent releases will further increase the atmospheric chlorine. If releases cease, the atmospheric chlorine will fall to half the peak level in 50 to 100 years. CFCs have been released for several decades at an increasing rate, so the atmospheric levels of inorganic chlorine from this source have already accumulated. In contrast, inorganic chlorine released in the stratosphere by a rocket results in an immediate increase in organic chlorine. The lifetime of this chlorine in the stratosphere is three to five years, depending on the altitude of release. This shorter lifetime means that atmospheric chlorine from rockets will peak in the year of release. If there are no further rocket releases of chlorine, the atmospheric chlorine from this source will drop to half the peak level in three to five years. Rocket launches using chlorine containing propellant have been occurring for more than a decade, so the atmospheric chlorine levels from this source have also been accumulating. The

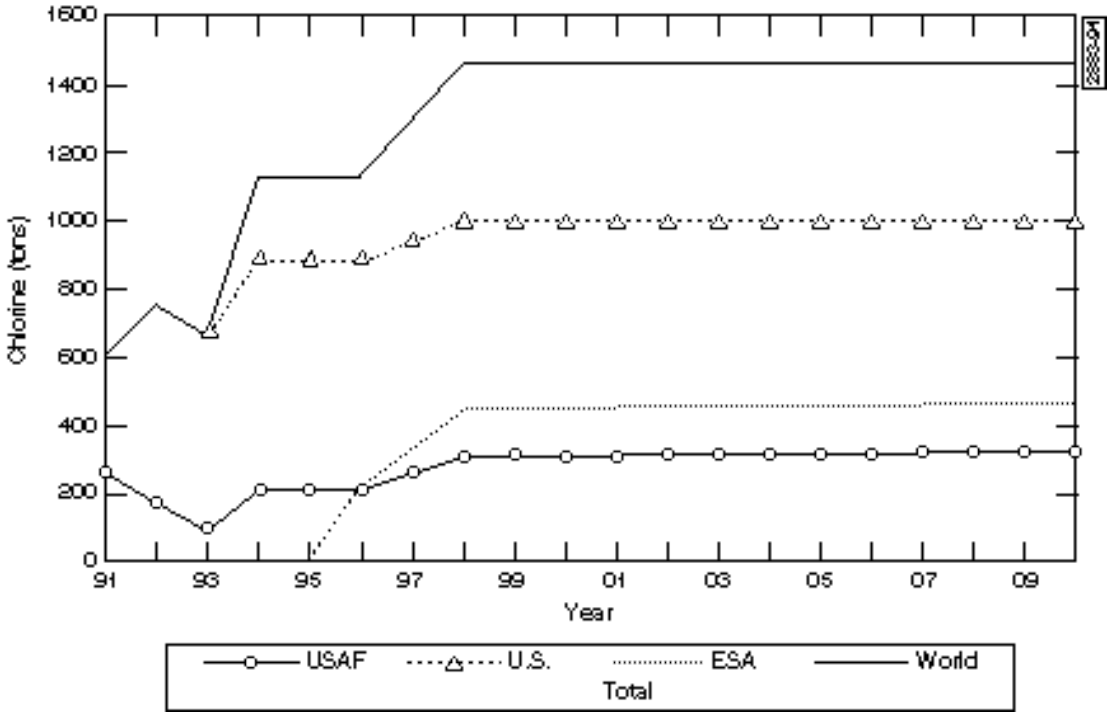


Figure 2. Total chlorine deposited in the stratosphere per year by all launches worldwide.

Figure 3. Total inorganic chlorine in the stratosphere.

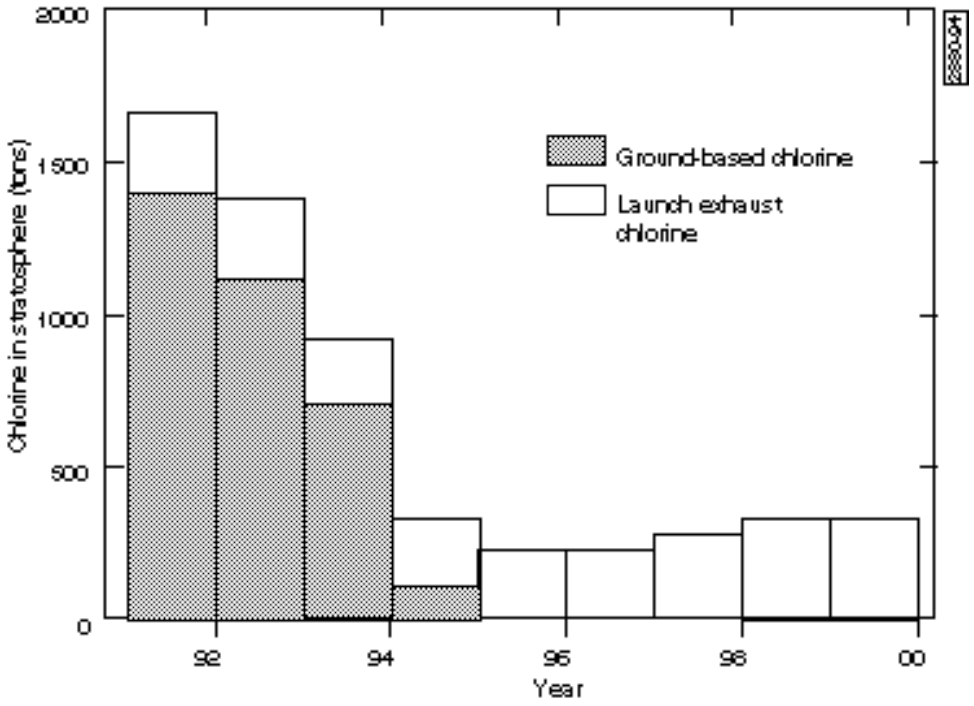


Figure 4. Chlorine from Air Force operations.

different lifetime of the sources is not apparent if you take the integrated effect over time. The integral of the atmospheric concentration of inorganic chlorine over time will be roughly the same for rockets and for CFCs. The total effects of equal masses of chlorine released as CFCs or as rocket exhaust will be roughly the same.

In Figure 5a, we show the impact of newly-released CFCs on the stratosphere. This gives the steady-state mass of inorganic chlorine in the atmosphere resulting from Air Force use of CFC after 1991. In the following equations, we put the mass of chlorine from CFCs on a basis for comparison with the mass of chlorine from solid rocket boosters.

The calculation of the numbers for Figure 5 is as follows. Let the concentration of inorganic chlorine, i.e., all chlorine species that result following the initial photolysis of a CFC, be $[C1_x]$. At steady state:

$$d\left[Cl_x\right]/_{dt} = production\_rate - loss\_rate = 0 \tag{14}$$

Production rate = Total mass of CFC chlorine in the atmosphere/total CFC lifetime:

$$production\_rate = \%Cl\frac{[CFC]}{\tau_{cfc}} \tag{15}$$

Loss rate = Steady state mass of inorganic chlorine/stratospheric lifetime of the active chlorine:

$$loss\_rate = \frac{[Cl_x]}{\tau_{clx}} \tag{16}$$

Equating and solving for the steady state mass of active chlorine:

$$[Cl_x] = \%Cl[CFC]\frac{\tau_{clx}}{\tau_{cfc}} \tag{17}$$

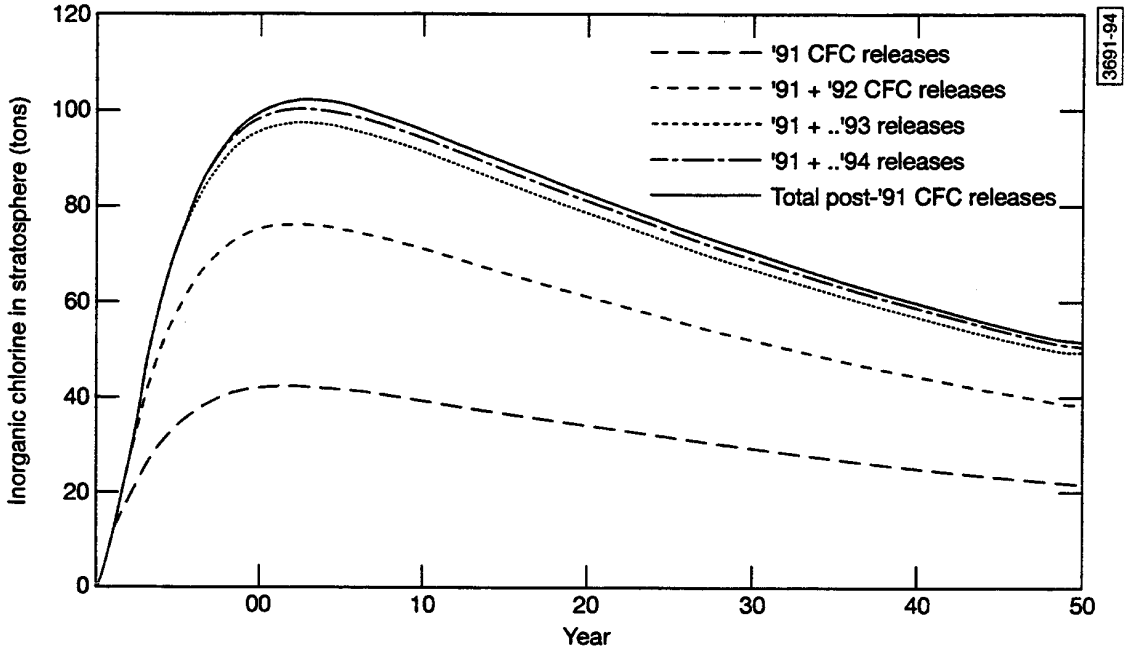
For a typical CFC, the lifetime is about 60 years, and we usually choose three years for the average lifetime of active chlorine in the stratosphere. CFC is typically about 60 percent chlorine (0.6 mass fraction). Therefore, the steady state mass of active chlorine is about 1/20 multiplied by 0.6, or about 3 percent of the total released mass of CFC.

In Figure 5a, the shape of the curve is taken from the Executive Summary of the WMO 1989 report. The curve shows the time dependence of atmospheric chlorine concentration following yearly injections of CFC-11, which has a characteristic lifetime of about 55 years. The size of the yearly releases is taken from Table 5. The peak of the curve is given by the steady-state calculation shown above; i.e., the CFC use for one year (1991) is roughly 1400 tons, and the peak concentration will be 3 percent of this, or about 42 tons. Because the lifetime is so long, successive injections of CFCs over a period of five years or so are essentially additive.

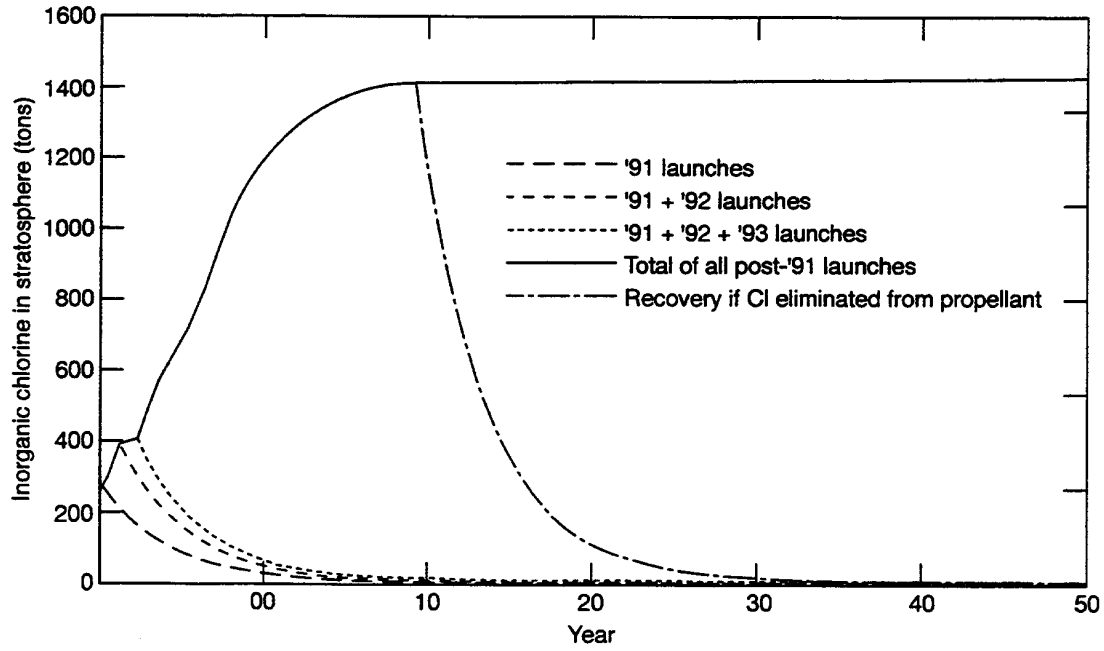
A similar analysis has been done for chlorine from rocket exhaust. In this case, the analogous production rate of inorganic chlorine is essentially instantaneous, but for this calculation we average all the launches over the course of a year and set the production rate to that amount per year. We have already corrected for the percent of chlorine in the exhaust, and 100 percent of the chlorine in the exhaust is inorganic. The rate at which the chlorine from rockets leaves the stratosphere may be a little slower than for CFCs since the solid rocket motors burn out at a higher altitude than the CFCs ever reach, but we will use three years as in the case for CFCs.

$$\frac{[Cl_x]}{1} = \frac{[Cl_x]}{\tau_{clx}} \tag{18}$$

During the year of launches, the production rate is always greater than the loss rate. In subsequent years the production rate is zero. In this case there is no true steady state; the peak concentration is in the year that launches occur, and is 100 percent of the inorganic chlorine injected in the stratosphere. Figure 5b shows the cumulative effect of successive years of launches beginning in 1991; the tons of chlorine injected each year is from Table 5. The chlorine recovery after a hypothetical sudden elimination of chlorine from rocket exhaust is also shown in Figure 5.



a. Effect of new Air Force CFC releases on chlorine loading



b. Effect of new Air Force launches on chlorine loading

Figure 5. Effects of Air Force activities on stratospheric chlorine loading.

It should be emphasized that due to enormous amounts of organic chlorine compounds used in the past and the longevity of these compounds, chlorine derived from this source will continue to dominate the stratospheric chlorine totals until at least the middle of the next century. However, given the extent of the ozone problem, new sources of chlorine may be given more attention than much larger releases were given in the past. Although individual launches may be negligible compared to the massive ODC releases from non-launch sources, and individual programs may have a small impact on stratospheric ozone each year, the total amount of launch activity worldwide should be regarded as a potentially significant factor. Further, recent comments[19] in Nature suggest that rocket launches will be considered in future legislation relating to stratospheric ozone depletion.

Reactions such as those described in Section 3 are analogous to the reactions that take place on polar stratospheric clouds to produce the Antarctic ozone hole, but they have not yet been examined in the laboratory. Such chemistry could potentially enhance either the local or global effects of solid rocket booster exhaust.

In conclusion, worldwide space launches currently contribute over 800 tons of chlorine and 1000 tons of alumina particles to the stratosphere annually. This represents 0.25 percent of the total inorganic chlorine produced in the stratosphere which meets with ozone. The 1991 Work Meteorological Organization Report [25] quoted several modeling studies of the global scale effects of rocket launches. These studies gave values of less than 0.1 percent total column ozone depletion in some cases, and a range of .0072 to .024 percent in other cases. The report acknowledges that the contribution of heterogeneous chemistry to these numbers is poorly understood, and requires more work. Reviews since the 1991 report [26] indicate that global ozone decreases are due to a complex interaction between homogeneous gas reactions, heterogeneous chemistry on existing aerosols, and mixing of severely ozone-depleted air from the poles. Such effects are not included in the rocket-related studies quoted in the WMO report. If alumina particles are shown to destroy ozone, the total launch impact on the ozone layer would increase. In addition, the small contribution of space vehicles to ozone depletion is increasing rapidly, and could double by the year 2000. Given these facts and the likely consequences for space launch operations, prudence dictates that more information be gathered on the interaction of rocket exhaust with the atmosphere so that launch systems can be developed based on consideration of cost, performance, reliability, and overall environmental impact.

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Appendix

Table 6 gives the chlorine deposited by several launch vehicles in vertical layers 5 km thick. These are typical results; specific flights may vary slightly depending on payload and individual motors. The results are presented graphically in Figure 5.

Table 6. Chlorine Deposited by Selected Launch Vehicles

	Chlorine (tons)			
Altitude (km)	Delta II	Atlas IIAS	Titan IV	Shuttle
5	10.68	4.01		
10	3.88	1.17		
15	2.17	0.94		
20	0.58	0.94	9.25	21.63
25	1.48	0.94	8.04	16.65
30	1.62	0.94	6.94	13.41
35	1.41	0.67	5.84	10.70
40	1.25	0.00	4.96	8.48
45	1.06	0.00	4.07	3.17
50	0.84	0.00	3.30	0.55
55	0.18	0.00	0.00	0.00

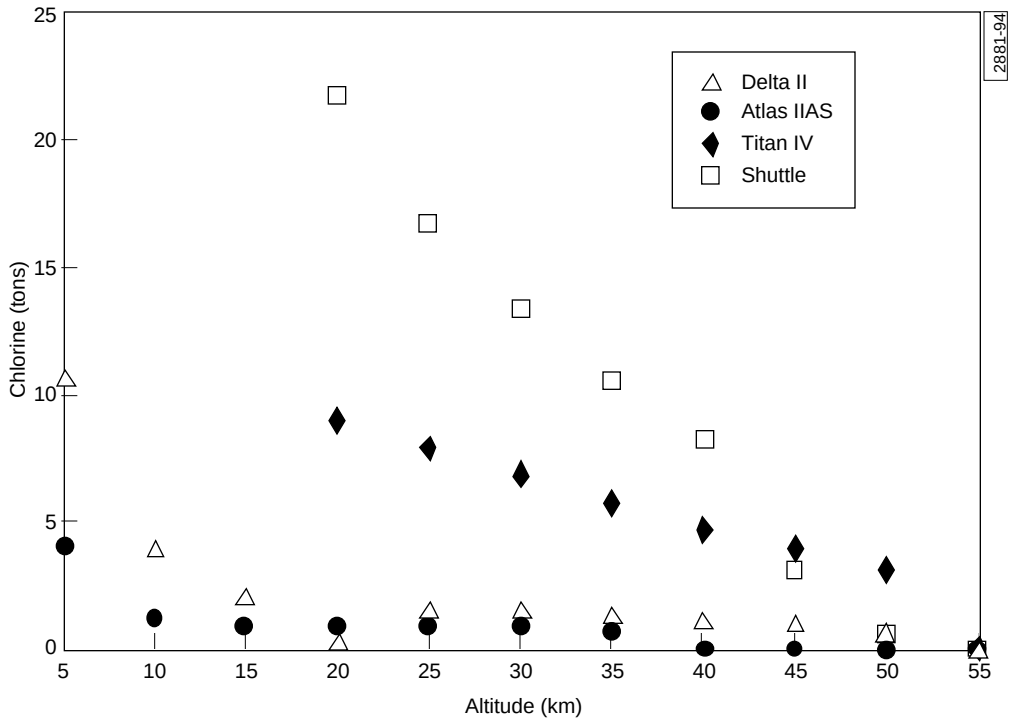

Figure 6. Total chlorine deposited by selected launch vehicles per atmospheric layer.